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# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Expandable Thermoplastic Polymer Particles containing Volatile Fluid Foaming Agent and method of making the same

We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to plastic particles. It more particularly relates to plastic particles which have incorporated therein a discrete liquid phase and to materials prepared therefrom.

One of the major disadvantages of the prior methods of making the foamed thermoplastic products known to the art is that inherently the cell size of the foamed plastic material is relatively large and that the particles themselves are not readily available commercially in sizes sufficiently small for some applications. In many instances it is desirable to have available an expandable thermoplastic resinous material which is capable of forming a unitary cellular body having a small cell size and capable of conforming to minute variations of a mold cavity. Further, it would be advantageous and beneficial to have available a thermoplastic resinous particle or bead which is capable of expanding into a single cell when required. It would also be beneficial if there were available a method of fabricating thermoplastic resinous

[Price 4s. 6d.]

particles having a generally cup-like or generally spherical urn-like configuration.

In accordance with this invention these benefits are achieved by providing a monocellular thermoplastic resinous particle having encapsulated therein a discrete portion of at least one non-polar liquid, volatile blowing agent for said thermoplastic resinous particle.

Further features and advantages of the invention will become more apparent from the following specification when taken in connection with the accompanying drawings wherein:

Figure 1 depicts a thermoplastic resinous particle in accordance with the invention;

Figure 2 illustrates a particle in accordance with the invention after heat-treating;

Figure 3 illustrates an alternative embodiment of a particle in accordance with the invention;

Figure 4 is a sectional view of a particle of Figure 3 after heating;

Figure 5 illustrates a sectional view of a particle in accordance with Figure 4 containing an additional feature;

Figure 6 is a sectional view of a body comprised of expanded particles of Figure 1;

Figure 7 depicts an article having a coating employing particles of the invention;

Figure 8 depicts a schematic enlarged sectional view of a coating such as in Figure 7; and

Figure 9 is a schematic enlarged sectional

view of the coating of Figure 8 in expanded form.

In Figure 1 there is illustrated a sectional view of a particle generally designated by the reference numeral 10. The particle 10 comprises the thermoplastic resinous, generally spherical shell 12. The shell 12 defines an outer spherical surface 14 and an inner spherical surface 15. Confined within the spherical surface 15 is a non-polar liquid blowing agent 17, and the blowing agent 17 fills a major portion of the cavity defined by the inner surface 15 and serves to partially define the vapor space 18. The particle 10 is of generally symmetrical spherical configuration having the inner surface 15 and the outer surface 14 in a generally concentric arrangement.

In Figure 2 there is illustrated a sectional view of a monocellular particle or monocell generally designated by the reference numeral 20 which comprises a body 21 of thermoplastic resinous material. The body 21 is in the form of a generally spherical shell having an outer surface 23 and an inner surface 24. The inner surface 24 defines a space 26. The particle 20 of Figure 2 is formed by heating a particle such as particle 10 of Figure 1 to a temperature sufficiently high to permit plastic flow of the wall 12 and to vaporize at least a portion of the blowing agent 17 sufficient to provide adequate pressure to deform the spherical shell 12 of Figure 1 into the shell 21 of Figure 2.

On cooling of the shell 21, the thermoplastic resinous material no longer will flow and deform and it retains its increased dimension, while the blowing agent tends to condense and results in a reduced pressure within the particle. Usually on expansion of a particle such as 10 into the configuration of the particle such as 20, the pressure within the space 26 will usually be less than the atmospheric pressure surrounding the outer surface 23 of the shell 21 and the wall thickness of the shell 21 then governs the rate at which the higher pressure atmosphere outside the expanded particle 20 diffuses through the wall and into the space 26. Frequently, the raising agent simultaneously diffuses out of the particle as the atmosphere or air surrounding the particle diffuses in. Generally, the expanded particles on storage tend to lose their blowing agent to the atmosphere.

In Figure 3 there is illustrated a sectional view of an alternative embodiment of the invention wherein a generally spherical particle 30 comprises a shell 31, defining a generally spherical outer surface 33 and an inner surface 34. The inner surface 34 defines a cavity or space 36 having disposed therein a non-polar volatile blowing agent 37 and a vapor space 38. The space 36 is not disposed concentrically with the outer surface 33, thus providing the shell 31 with a heavy or thick wall portion 39 and a thin wall portion 40. The particle 30, on heating to a temperature sufficiently high to

promote plastic flow in the shell 31 and to volatilize the blowing agent, forms a particle such as particle 45 of Figure 4.

Figure 4 is a sectional view of a particle 45. The particle 45 has a generally spherical cup-like configuration. The body portion 46 defines an exterior surface 47 and an interior surface 48. The exterior surface 47 and the interior surface 48 define an opening 49 to the space 50.

In Figure 5 there is illustrated a sectional view of a particle generally indicated by the reference numeral 55 which is similar to the particle 45. The particle 55 has a wall portion 56 defining an interior cavity 57 and an opening 58. Disposed within the cavity 57 is a liquid 59. The liquid 59 suitably may be any desired material which is non-reactive with or a non-solvent for the thermoplastic resinous material of the particle 55.

In Figure 6 there is depicted a sectional view of a body 62 of particles 63 which are formed by the simultaneous expansion and adherence of the particles 63 to their adjacent neighbors.

In Figure 7 there is illustrated an article or container generally designated by the reference numeral 70. The container 70 comprises an exterior wall portion 71 defining a cavity 72. Disposed peripherally about the wall portion 71 is an adherent coating 73 containing a plurality of expandable thermoplastic resinous particles having encapsulated therein a liquid blowing agent. (Relative size of particles is greatly exaggerated for clarity).

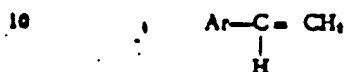
In Figure 8 is an enlarged schematic cross sectional view of a substrate 80 having on one surface thereof a coating 81. The coating 81 comprises a thermoplastic resinous binder having contained therein a plurality of expandable particles.

Figure 9 depicts an enlarged schematic sectional view of a substrate 80 having on one major surface thereof a coating 81' comprising a binder 82 adhering together a plurality of particles 20. The coating 81' of Figure 9 is readily achieved by heating the coating 81 of Figure 8 to a temperature at which the particles as shown in Figure 8 expand to form the particles 20.

Particles in accordance with the invention are readily prepared from a wide variety of materials. Advantageously, the particles in accordance with the invention are usually prepared by providing an aqueous dispersion of (1) organic monomeric materials suitable for polymerization to a thermoplastic resinous material having the desired physical properties, (2) a non-polar liquid blowing or raising agent which exerts little solvent action on the resulting polymer, which is employed in a quantity in excess of that which is soluble in the polymer, and (3) a dispersion stabilizing material which is utilized to maintain the dispersion, subsequently polymerizing the monomeric

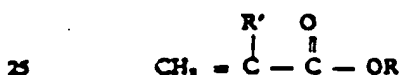
material to solid spherical particles having a quantity of the liquid blowing agent encapsulated therein as a distinct and separate phase.

A wide variety of organic materials may be employed with advantage in the practice of the invention. Typical of these are the alkenyl aromatic monomers. By the term "alkenyl aromatic monomers" is meant a compound having the general formula:



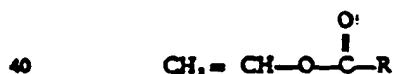
wherein Ar represents an aromatic hydrocarbon radical or an aromatic halo-hydrocarbon radical of the benzene series. Examples of such alkenyl aromatic monomers are styrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, ethylstyrene, *ar*-vinyl-xylene, *ar*-chlorostyrene or *ar*-bromostyrene. Various other styrene derived compounds may be employed such as vinylbenzylchloride and *p*-tert-butylstyrene.

The acrylate monomers alone or in combination with the alkenyl aromatic monomers may also be utilized. Such acrylate-type monomers include monomers of the formula:



wherein R is hydrogen or an alkyl radical containing from 1 to 12 carbon atoms and R' is hydrogen or methyl. Typical acrylate materials which may be used are methyl methacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, butyl methacrylate, propyl methacrylate, lauryl acrylate, 2-ethylhexylacrylate, and ethyl methacrylate.

Copolymers of vinyl chloride and vinylidene chloride, acrylonitrile with vinyl chloride, vinyl bromide, and similar halogenated vinyl compounds may be incorporated in compositions in accordance with the invention. Esters, such as the vinyl esters having the formula:



wherein R is an alkyl radical containing from 1 to 17 carbon atoms, may also frequently be employed with benefit. Typical monomers falling within this classification are vinyl acetate, vinyl butyrate, vinyl stearate, vinyl laurate, vinyl myristate, and vinyl propionate.

Beneficially, in certain instances and when using specific dispersing agents, it is frequently advantageous to incorporate in the polymeric material a portion of a copolymerizable acid to further improve the geometric form of the particles in accordance with the invention and oftentimes provide increased adhesion of the

resultant polymeric particles to various polar surfaces such as metal and wood.

Typical copolymerizable acids are acrylic acid, methacrylic acid, itaconic acid, citraconic acid, maleic acid, fumaric acid, and vinylbenzoic acid.

A wide variety of non-polar blowing or raising agents may be incorporated within the polymerization system. They can be volatile fluid-forming agents such as aliphatic hydrocarbons including ethane, ethylene, propane, propene, butene, isobutene, neopentane, acetylene, hexane, heptane, or mixtures of one or more such aliphatic hydrocarbons having a molecular weight of at least 26 and a boiling point below the range of the softening point of the resinous material when saturated with the particular blowing agent utilized.

Other suitable fluid-forming agents are the chlorofluoro-carbons, e.g.  $\text{CCl}_4$ ,  $\text{CF}_4$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CClF}_3$ ,  $\text{CF}_3\text{CF}_2\text{F}$ , and

$\text{CF}_3\text{CF}_2\text{CF}_2\text{F}$  and tetraalkyl silanes such as



tetramethyl silane, trimethylethyl silane, trimethylisopropyl silane and trimethyl-*n*-propyl silane. The boiling point of such blowing agents at atmospheric pressure should be in about the same temperature range or lower than the softening point of the resinous material employed.

Suspensions of monomeric materials for the preparation of particles in accordance with the invention are usually made employing a suspending agent such as water-soluble gum e.g. methyl cellulose, gum bar, hydroxypropyl methylcellulose, carboxy methylcellulose, colloidal silica, and colloidal clays.

Usually, in order to initiate polymerization, a suitable catalyst, preferably of the oil-soluble variety, is incorporated within the monomeric system. Suitable catalysts include peroxide compounds and high energy ionizing radiation. Suitable organic peroxides include benzoyl peroxide, lauryl peroxide, tert-butyl peracetate, tert-butyl perbenzoate, cumene hydroperoxide, and cumene ethyl peroxide.

In preparing the particles in accordance with the invention, it is desirable, although not necessary, to exclude oxygen and similar free radical chain-terminating materials from the system. This is readily accomplished by flushing the system with an inert atmosphere such as nitrogen.

Generally, in preparing the aqueous dispersions to be polymerized in accordance with the invention, the monomer and blowing agent constitute a major portion of the oil phase and are incorporated with water in a ratio of from 1:1 oil-phase-to-water to 1:6. Usually, the suitable dispersing agent is incorporated within the water phase and the monomer, blowing agent, and catalyst are mixed. It is beneficial

to provide violent agitation if the resultant particles are desired to have a small diameter.

If extremely small particles are desired, it may be necessary to use a homogenizer or similar device in order to obtain uniform control of particle size. It is frequently beneficial to utilize a limited coalescence technique as described in Specification 802,061 in combination with a mechanical homogenizer or similar devices that will subject the dispersion to conditions of high shear prior to polymerization. Using a limited coalescence technique droplets may be produced having a particle size of from  $\frac{1}{2}$  to 50 microns.

There are various additaments which may be made to the polymerization system. Encapsulation of a blowing agent may be obtained where the initial monomer charge contains a polymer dissolved therein, for example, 10—15 percent by weight polystyrene is readily dissolved in methyl methacrylate and is polymerized in accordance with the examples of this application. Stabilizers, lubricants and similar substances, which oftentimes are desirably incorporated into polymeric materials may be added with the monomer or blowing agent as desired.

The order of the addition of the constituents to the polymerization usually is not critical, but beneficially it is more convenient to add to a vessel the water and dispersing agent, then add the blowing agent to the monomer, and incorporate the oil-soluble catalyst in the monomer mixture, and subsequently add with agitation the monomer phase to the water phase. The blowing agent or raising agent must be present in a proportion which exceeds the solubility of such an agent in the polymer formed. The proportion of blowing agent usually is about 20 to 30 weight per cent and, beneficially, is not less than about 20 e.g. from 20 to 95 and preferably from 50 to 95, volume percent based on the total volume of the polymer and blowing agent. When suitable blowing agents having desirable solvent characteristics for the monomer system being utilized are employed in quantities less than 20 volume percent, that is, based on the volume of the oil phase, separation frequently fails to occur and particles smaller in diameter than about 40 microns do not expand on heating.

Generally, for most applications, it is desirable to prepare a bead having an extremely small diameter such as from 1 micron to 50 microns and, advantageously, between 2 and 10 microns. Such beads or particles having a small diameter are readily molded into shaped articles having a smooth uniform texture, excellent insulation value, and high strength. Small particles are readily dispersed in gases such as air to prepare plastic smoke or fog. However, if desired, larger particles are readily prepared by utilizing a suitable suspending agent. Beneficially, on polymerization of a droplet of the desired size, the monomer, or monomers, as

the case may be, polymerize to form a polymer shell such as the shell 12 of Figure 1 surrounding a distinct and separate liquid phase of the blowing agent which is forced out of the monomer-blowing agent mixture of the bead as polymerization progresses.

Generally, in order to prepare the symmetrical beads as shown in Figure 1, it is desirable to incorporate within the monomer mixture copolymerizable polar systems, for example, if a non-polar monomer is being polymerized such as styrene, in order to assure that a majority of the particles produced from the polymerization have a uniform wall thickness, it is generally desirable to incorporate from 1 percent by weight of the monomer to 10 percent by weight of the monomer of a copolymerizable polar system such as methyl methacrylate, acrylic acid, fumaric acid, and vinyl acetate.

When polymeric materials are utilized which have softening points below 50°C., such as polyacrylates or acrylate copolymers which have a plasticizing monomer incorporated therein such as 2-ethylhexylacrylate, careful handling of the product is required. After polymerization in a pressure vessel if the product is to be isolated as an unexpanded particle the temperature of the reaction mixture, and the atmosphere in which it is being handled, must be at least 5° below the softening temperature of the polymer. Otherwise, expansion will occur when the pressure is released from the polymerization vessel. In many instances where the desired product is the expanded bead, the polymerization vessel may be vented at a temperature above the softening temperature of the polymer and a slurry of expanded particles obtained which are readily separated from the liquid by flotation and dried by centrifugation and similar conventional methods.

The copolymers of styrene with from 1 to 4 percent by weight methacrylic acid, and the copolymers of styrene with 10 to 80 percent acrylonitrile are particularly advantageously employed. These compositions, when polymerized in accordance with the invention, provide a product which consists of about 100 percent spherical particles having symmetrically encapsulated therein a blowing agent. Also advantageous are those styrene copolymers which provide symmetrical encapsulation in at least 80 percent of the particles prepared. These polymers are copolymers of styrene with from 15—40 percent by weight of vinyl benzyl chloride, also copolymers of styrene and from 1 to 8 percent by weight of acrylic acid. Copolymers of styrene and 2—10 percent of acrylonitrile also provide a product which shows over 80 percent symmetrical encapsulation. At least 80 percent symmetrical encapsulation is achieved in utilizing a polymer of acrylonitrile with from 7 to 60 percent by weight of vinylidene chloride. Vinyl benzyl chloride and copolymers of ortho-chlorostyrene

with from 1 to 8 percent of acrylic acid also provide symmetrical encapsulation. Typically, if particles generally in accordance with Figure 5 are to be prepared, it is advantageous to utilize monomers such as styrene which results in a major portion of the resultant particles having an asymmetric encapsulation which, on heating to a suitable temperature, form generally cup-like particles of Figure 4.

Particularly beneficial and advantageous for the preparation of spherical particles having a blowing agent symmetrically encapsulated are such monomer compositions as methyl methacrylate, copolymers of methyl methacrylate containing up to 20 percent by weight of styrene, copolymers of methyl methacrylate and up to 50 percent by weight of the comonomers of ethyl methacrylate, copolymers of methyl methacrylate, and up to 70 percent by weight of ortho-chlorostyrene. These compositions, when utilized in accordance with the invention, provide a product which consists substantially of 100 percent of the particles showing symmetric encapsulation. Also advantageous and beneficial are those compositions which provide a product which has an excess of 80 percent of the product as symmetrically encapsulated blowing agents. Methyl methacrylate materials comprising 10 percent by weight of acrylonitrile, copolymers of methyl methacrylate containing up to 20 percent paraterdiarybutylstyrene, polymers of methyl methacrylate with up to 40 percent vinyl acetate, and polymers of methyl methacrylate with up to 20 percent butyl acrylate can be used.

Frequently it is beneficial to utilize in the practice of the present invention a di-functional monomer or cross linking agent which serves to increase the melt or flow viscosity of the polymeric composition at temperatures sufficiently high to cause volatilization of the blowing agent and subsequent deformation of the originally formed sphere into a larger hollow sphere.

In the preparation of expandable particles in accordance with the invention, usually it is most advantageous to prepare them by polymerizing the monomeric materials to a relatively low molecular weight if maximum expansion of the particles is desired. For example, greater expansion under similar conditions will be obtained from particles prepared utilizing 4 percent by weight based on the monomer of a free radical generating catalyst than if one percent by weight of the catalyst is employed. The lower molecular weight material usually tends to expand to greater volume than does the higher molecular weight material. This is presumed to be due to the difference in the flow characteristics of the thermoplastic resins as the molecular weight varies. If the polymerization conditions are such that a cross linked non-thermoplastic resin

is prepared there can be little or no expansion. If the opposite extreme of molecular weight is employed wherein a very low molecular weight resin is utilized, expansion can occur but the product usually is of relatively low strength and oftentimes of limited value. If the diffusion rate of blowing agent through a polymer varies with the composition of the polymer as well as its molecular weight, the optimum quantity of blowing agent to be incorporated within a particular particle for expansion will vary accordingly. Thus, if particles of a given diameter are prepared, some from a polymer having a relatively high diffusion rate of the blowing agent through the cell wall, a greater quantity of blowing agent will be required than in a particle of similar dimensions and having similar thermoplastic properties. This optimum ratio will vary as the particle diameter varies.

A small particle will generally require a larger quantity of blowing agent than will a larger particle as the thickness of the wall initially is thinner. Thus the diffusion rate through the wall of a small particle having a given polymer to blowing agent rate ratio is significantly greater than that for a particle having 3 or 4 times its diameter. Thus in the instance of particles having a relatively high percentage of blowing agent which are small in diameter substantially less expansion can be expected than for a particle initially containing less blowing agent and more polymer. That is, the optimum polymer raising agent ratio for each polymer blowing agent combination is dependent on particle size. For example, methyl methacrylate particles containing nroptane and having a diameter of about 10 microns have for optimum expansion approximately a ratio of 1:1 blowing agent to polymer.

However, frequently it is desirable to prepare particles which do not expand to give a symmetrical particle such as is illustrated in Figure 2 and it is desired to prepare expanding particles wherein the liquid occlusion is not centered within the drop but disposed more toward one side of the particle. This is most readily accomplished by utilizing a polymerization system employing non-polar monomers. The non-symmetrical particles, such as are illustrated in Figure 3, are particularly desirable and advantageous for the preparation of the expanded urn-like bodies of Figure 4. The urn-like bodies provide an extremely small receptacle which is readily filled with a liquid or liquid dispersion, subsequently dried by conventional means such as centrifugation and the judicious application of warm air to result in a body such as is illustrated in Figure 5, wherein a liquid is incorporated within the cavity is open and exposed to the atmosphere, and yet the outer wall of the particle is dry. Thus, there is provided a unique and beneficial carrier for liquids which may be handled in the form of a substantially free-flowing powder

and is particularly advantageous for the incorporation of additaments into plastic masses in which the additament oftentimes is not readily dispersible and yet substantially uniform dispersion is required. Such particles also serve other unique functions such as dye carriers wherein a dispersion of the dye in a liquid is incorporated within the cavity, the particles dried to remove all moisture, and the outer surfaces polished by tumbling, thus resulting in a mass of small particles each containing a portion of dye and presenting a clean exterior surface. If such dye is a water-soluble dye, the particles are readily added to water and the dye readily dissolved therefrom.

Expanded beads or particles preferably those having diameters of 0.5 to 2.0 microns in accordance with the present invention are readily incorporated in coatings. This oftentimes is more readily done by prefoaming or expanding the beads into individual spherical particles and subsequently admixing them in a suitable binder. Such a binder can be one of the lacquer type, that is a binder dissolved in a solvent, or it can be an aqueous dispersion of a film forming polymeric material or even an aqueous solution of a film forming material. The precise and particular type of binder or vehicle for the expanded particles will depend upon the particular composition of the expanded particle which is utilized. Generally the vehicle should be of such nature that it does not chemically attack or physically deform the expanded particles and allows them to remain in the finished coating as distinct physical entities. The relative amount of the binder employed in the vehicle will be dependent upon the properties desired in the resultant coating. For example, if a porous bulky coating is desired the proportion of binder is maintained sufficiently small that the particles are adhered together primarily at their points of contact and insufficient binder is provided to fill the interstitial spaces between the particles. If an impervious coating is desired a larger quantity of binder is employed which results in a plurality of hollow spherical particles dispersed within a matrix of the binder. In choosing a vehicle for a particular polymeric composition of expanded bead it is necessary that the vehicle should not exert a strong solvent action upon the particle. Otherwise the insulating and other desirable properties of the coating which are achieved by using the hollow beads is destroyed and the resultant coating will be no more than that which is achieved by dissolving an equivalent amount of polymer in the vehicle and depositing it as a lacquer or crushing the beads prior to dispersal in the vehicle. Coatings which utilize the hollow spheres tend to be excellent light dispersing media as they provide a large number of internal surfaces, each of the surfaces being curved.

Suitable coatings formulated with expanded

particles in accordance with the invention provide thermal insulation as well as a generally attractive appearance. The thickness to weight ratio of such coatings is generally substantially and significantly greater than usual coating materials thus providing insulation and resistance to degradation by sunlight and similar radiation. Beneficially temporary coatings are easily prepared by utilizing a water soluble binder. By way of illustration the expanded particles may readily be dispersed in an aqueous system utilizing a water soluble polymeric material. For example, expanded particles in accordance with the invention are readily dispersed in an aqueous system containing a water soluble polymeric material such as water soluble hydroxypropyl methyl cellulose, sodium carboxy cellulose, and gum agar. As with other coatings utilizing the particles of the invention it may be applied by spraying, dipping, rolling, brush and the like and on drying provides thermal insulation as well as protection from radiation. However, when the coating is no longer it is readily removed by flushing with water. Among the permanent coatings one may utilize a solution of a thermosetting material such as a phenol formaldehyde resin in water or suitable solvent which provides a coating that is not readily attacked by either water or organic solvents. Such insulating coatings are advantageously used in many applications including piping, duct work, walls, and the like. The water soluble coatings may be utilized for temporary frost protection on plants such as fruit trees and flowers.

Alternatively the unexpanded particles are readily incorporated into a suitable vehicle containing a binder which must meet the limitations of a vehicle for expanded particles but in addition must be thermoplastic. Where the unexpanded particles are employed, in a coating with thermoplastic binder, heating of the dried coating causes the particles to expand and provide a foamed coating. Advantageously such an expandable coating can readily be used in a wide variety of applications including insulating laminated bags, frozen food containers, ice cream and cold drink containers as well as hot drink containers. Such foamable coatings are particularly advantageous and beneficial where an attractive texture effect is desired, as they are readily applied in such a manner as to give a non-uniform coating thickness; for example, if they are incorporated in a latex paint formulation and applied to a surface utilizing a roller having a long nap, the coating has a short term variation in thickness which on expansion gives rise to a corresponding variation in the expanded thickness of the coating. The binders utilized with the expandable particles in accordance with the invention must be thermoplastic within a temperature range suitable to the particular particle employed.

That is, for example, if a thermoplastic resinous particle containing as a distinctly separate liquid phase an expandable liquid or blowing agent is placed within the coating which has a softening point which is substantially less than that of the particle, that is from about 70—100°C. lower than the softening point of the particle resin a relatively poor foamed coating will result. In such a case the temperature required to promote expansion or release of blowing agent by the particles is sufficiently high that the viscosity of the binder oftentimes will be too low for satisfactory foaming to occur. Because of the relatively low viscosity at the high temperature the blowing agent which is released from rupturable particles in accordance with the invention diffuses rapidly through the binder material as it is cooling and the resultant foam volume is generally less than that which could be obtained if a more suitable binder were utilized. Although this is beneficial, certain exceptions exist, particularly in some of the plasticized polyvinyl chloride compositions which are relatively impervious to the blowing agent and whose flow viscosity does not change as rapidly with temperature as do binders such as the vinylidene chloride — vinyl chloride compositions. The expandable coatings and coatings containing expanded particles are readily applied by the common coating techniques. In coatings where the expanded particles are utilized some precautions must be observed to maintain uniformity of the coating composition as the hollow particles exhibit a tendency to float. This tendency to stratify is somewhat less than might be generally presupposed particularly in cases where the diameter of the particles is relatively small, that is, below 50 microns. The viscosity of such coating mixtures and Brownian movement tends to make stratification a slow process. Usually in the preparation of expandable coatings in accordance with the present invention it is desirable to maintain a sufficient quantity of binder in the coating then on expansion it will remain a coherent, adherent protective layer. However, by reducing the volume of the binding material to a point where it is sufficient to bind the unexpanded particles but insufficient to bind the expanded particles, a coating composition of this type provides an excellent temporary coating which can readily be removed by the application of heat. By way of illustration, if a metal surface is to be protected by a temporary coating which is to be removed without the application of solvent or other liquid means a coating of expandable particles in sufficient binder to maintain a coherent coat is applied to the surface. When the coating is to be removed the temperature is raised to the point where the spherical particles expand. If a relatively non-polar binder is employed, that is, one with less than maximum possible adhesion to the metal substrate, the binder will

preferably adhere to the particles as they expand. As the volume of the binder present is insufficient to maintain a coherent film and the coating falls away as a dust leaving a clean metallic surface, the expandable coatings of the present invention inherently are intumescent. If a raising or expanding agent such as a halogenated compound is employed significant fire retardant properties are introduced. The foamable coatings prepared utilizing halogenated materials, are found to be excellent fire retardants.

Coating compositions utilizing expandable particles are also beneficially employed for the fabrication of laminates. For example, a laminate is readily prepared by coating a paper with an expandable coating, positioning the two portions of the coated paper with their coatings in contact and heating the sheets to a temperature sufficient to cause the coatings to expand and fuse together. The resultant laminate is strong, light in weight, and exhibits excellent insulating properties. Similar laminates are readily prepared utilizing metallic foils, synthetic resinous film, various papers, wood veneer, and the like. Sheets having an expandable coating in accordance with the present invention may be treated by the selective application of heat to provide various decorative patterns. For example, a sheet of material having an unfoamed coating on the surface may be selectively treated with heat to prepare limited and patterned foamed portions. This is readily accomplished by using a heated stylus applied to the surface of the coated sheet remote from the coating or by the application of a heated patterned platen. Various designs and indicia are readily generated. Particularly advantageous is the use of a colored base sheet employing a clear coating formulation. On heating, the foamed portions appear white or slightly tinted with the color of the base sheet and stand out in sharp contrast thereto. Alternatively a colored coating composition may be used and on foaming the intensity or depth of the color is greatly reduced. Alternatively, a foamed coating may be treated by the selective application of heat to emboss it and generate decorative patterns. For example, if a sheet having a foamed coating thereon has a black surface underneath the foam it will appear white, provided of course the foam is of adequate thickness. On the application of a heated stylus or heated type the foam particles collapse and the coating is clear and the result appears as a black on white.

The expandable particles of the present invention are also advantageously employed in admixture with heat setting adhesives, particularly when adhesives are utilized on relatively uneven surfaces such as wood. When the adhesives containing a portion of the expandable particles are placed between two surfaces to be joined and heat applied thereto the expansion of the particles increases the



bulk of the adhesive and forces it into contact with the surfaces to be joined. Thus the advantages of conventional foaming adhesive technique are gained with the additional benefit that the adhesive may be applied in thin layers and still expand in the desired location. In a similar manner the expanded coatings may be utilized as adhesives themselves. If a tape or sheet is coated on both sides with expandable coatings and positioned between surfaces to be joined, heat applied, the particles expand, bond together and to the surfaces, thus providing in effect not only an adhesive but a gasket. Advantageously the expandable particles of the present invention may beneficially be employed for the preparation of expandable resinous compositions. If expandable particles of the present invention are incorporated into a self-reacting material which is exothermic, the heat of the reaction may be sufficient to expand the particles while the exothermic resinous substance is curing, thus low density foamed resinous material is readily prepared from materials which are not easily or readily foamed by conventional methods. As can be readily realized, the amount of heat liberated by the reactive exothermic material will control in part the amount of expansion. If with the chosen composition the degree of expansion is not as much as could be reasonably expected it may be desirable to raise the temperature of the resin forming material prior to its expansion. Particularly advantageous and beneficial as exothermic matrix within which to incorporate the particles of the present invention are the epoxy resin systems. Heretofore there has been no convenient manner in which rigid or flexible epoxy resin foam could be generated having a low density such as in the range of 1—3 pounds per cubic foot (16—48 kgs./cu.m.) without the use of pressure equipment to restrain the mixture until foaming is desired. Utilizing the particles of the present invention, a curable epoxy resin mixture may be filled with expandable particles of the present invention, then suitable hardener may be incorporated to cause the epoxy resin to react and generate sufficient heat to expand the particles and cure into a rigid body. Alternatively advantageous and beneficial compositions are achieved when less exothermic materials are employed. For example, if an epoxy resin formulation is prepared which cures only to the B stage, that is, it is solid thermoplastic and will cure to a cross-linked material on further heating, a powder can be obtained which may be used in fluid bed coating or sprayed on to hot surfaces where it will expand on the application of heat. Advantageously, epoxy resin expandable particle compositions are particularly useful for encapsulation of structures such as electronic circuitry and the like. Epoxy resin foam compositions prepared utilizing the particles of the present invention have low dielectric constants, that is, in the range of about 1.07 to 1.08, a satisfactory dissipation factor for most applications, that is, a dissipation factor of about 0.0025 and a volume resistivity substantially greater than  $10^{11}$  ohms cm<sup>3</sup>. Expandable coatings in accordance with the present invention are advantageously utilized in the preparation of cups for hot drinks and the like. Such cups are readily prepared by coating the paper from which the cups are to be prepared or alternatively coating the cups after fabrication. By utilizing an aqueous dispersion of a film forming latex together with the expanded particles of the invention, cups may be prepared which are readily stackable and occupy little if any more space than is normally occupied by conventional paper cups. Usually cups having a foamable coating may be fabricated from lighter paper or plastic, that is, thinner paper or plastic and consequently weigh less and occupy less space. Cups having an expandable coating are readily prepared for service by subjecting to heat immediately prior to use and after they are unstacked. One particularly advantageous embodiment of the invention incorporates a cup formed from a thin wall sheet and having on at least a portion of its outer surface a coating which will foam at a temperature of about 55°C. With a coating of this nature it is possible to expand the coating to give an insulating layer by a simple addition of a heated liquid to the container. Thus in a dispenser for hot beverages such as coffee, it is only necessary that the hot liquid be added to the cup in order for the insulating coating to appear. The disadvantages of a prefoamed coating are avoided as the necessity of pre-treating the cups in an oven or the like prior to serving. Generally low temperature foaming coatings are most advantageously prepared utilizing either the particles showing symmetrical encapsulation or asymmetrical encapsulation together with a film forming lacquer or preferably an aqueous latex of a film forming polymer which has a relatively low transmission rate for the volatile expanding agent utilized in the particles.

Beneficially, expandable or blowing agent containing particles which are relatively soft and indeed which may never exist under normal ambient conditions as individual discrete expanded bodies at a temperature above their softening point are readily utilized. Typical compositions which are beneficially employed for this application are those polymethyl acrylate, methyl methacrylate-methyl acrylate copolymers in about a 1:4 ratio in the copolymer and utilizing neopentane as a blowing agent, styrene butadiene copolymers having from about 20—60 parts of styrene and about 80—40 parts butadiene and the like. The softer copolymers generally do not have extended shelf life or stability, that is, there is a relatively rapid tendency of these compositions to lose their blowing agent to the surrounding

atmosphere. However, when admixed with a material such as vinylidene chloride, copolymers such as those film forming materials containing from 50—95 percent vinylidene chloride with another monomer copolymerizable therewith, very satisfactory expandable coatings are obtained. The softer materials also provide foamable coatings if extreme shelf stability is not required. Such particles, although not readily expanded as individual particles when deposited on a convenient substrate form a continuous film which, on further heating, will form a foamed coating.

Advantageously expandable thermoplastic resinous beads having a non-polar volatile liquid incorporated therein may be utilized as a means of handling or adding a volatile component to another system. For such applications, it is generally advantageous to maintain as high a proportion by weight of the encapsulated blowing agent in the particles as is possible. Beneficially, such particles are prepared in a substantially identical manner with the exception that considerably less polymerizable monomer is utilized. The precise proportion of polymer to volatile liquid employed will depend to a major extent on the desired size of the particle and the diffusion rate of the blowing agent through the particle wall. If the particles are to be utilized in such a manner that they are transferred directly from a sealed container to a suitable system such as, for example, if they are being added to a resinous matrix such as an epoxy resin, the diffusion rate of the blowing agent from the bead in a normal atmosphere may be relatively high as the time required to transfer particles from the sealed container to their ultimate destination will be small and any blowing agent loss will be proportionately low. However, if longer term shelf stability is desired or necessary the polymer shell must be proportionally thicker for a given resin and offer suitable resistance to the diffusion of the blowing agent from the particle. Oftentimes it is advantageous to utilize larger particles, that is, in the 50—1000 micron range; for such applications, the larger particles require less polymer per unit volume of blowing agent for identical loss of blowing agent rates.

Generally, in preparing particles with high proportions of blowing agent, that is, in excess of 50 percent, and more particularly in the range of 75—95 percent by volume of blowing agent, it is often desirable to employ a monomer system which on polymerization results in a cross linked polymer shell. Such systems contain up to 10 parts of a crosslinking agent such as divinyl benzene, propylene glycol dimethacrylate or diallyl phthalate. Contrary to the normal expectations, such copolymers are generally not rigidly cross linked, and on heating are capable of expansion. However, usually

they do not expand to the same degree as a material without the difunctional monomer.

The invention is further illustrated, but not limited, by the following examples. Example 44 is inserted for comparison purposes.

#### EXAMPLE 1

A polymerization reactor equipped with an agitator was charged with 100 parts of deionized water and 15 parts of a 30 weight percent colloidal silica dispersion in water. The colloidal silica dispersion was 30 weight percent solids and available under the Registered Trade Mark of "Ludox HS". To this mixture was added 2.5 parts of a 10 weight percent aqueous solution of a copolymer prepared from diethanol amine and adipic acid in equimolar proportions by carrying out a condensation reaction to give a product having a viscosity of about 100 centipoises at 25°C. One part of a solution containing 2.5 weight percent potassium dichromate was added. The pH of the aqueous solution was adjusted to 4 with hydrochloric acid. Methyl methacrylate was utilized as the monomer. An oil phase mixture was prepared utilizing 100 parts of methyl methacrylate and containing 20 weight percent neopentane (27.6 volume percent based on the total volume of the monomer-neopentane mixture) and 0.1 part of benzoyl peroxide as a catalyst. The oil phase mixture was added to the water phase with violent agitation supplied by a blade rotating at a speed of about 10,000 rpm. The reactor was immediately sealed and a portion sampled to determine the particle size. The droplets appeared to have diameters of from 2 to 10 microns. After the initial dispersion, the reaction mixture was maintained at a temperature of about 80°C. for a period of 24 hours. At the end of this period, the temperature was lowered and the reaction mixture had the appearance of white, milky liquid similar to a chalk-white milk. A portion of the mixture was filtered to remove the beads and the beads subsequently dried in an air oven at a temperature of about 30°C. A portion of the dried beads were heated in an air oven at a temperature of 150°C. for about 3 minutes. Upon heating, the beads showed a marked increase in volume. Microscopic examination of the beads prior to foaming indicated beads having diameters of from about 2 to about 10 microns and having dispersed therein a distinct spherical zone which appeared to contain liquid and a small vapor space. The beads which had been heated were examined microscopically and were found to have diameters of from about 2 to 5 times the diameter of the original bead and to have a relatively thin, transparent wall and a gaseous centre, i.e., a monocoil.

Following the procedure of Example 1 the following products were prepared:

Example	Monomers	Parts	Blowing Agent	Volume Percent	Result
2	Methylmethacrylate (MMA)	80	Neopentane	27.5	Symmetrical beads
	Styrene	20			
3	MMA	90	Neopentane	31.3	Symmetrical beads
	Ethyl methacrylate (EMA)	10			
	Divinyl benzene (DVB)	0.05			
4	MMA	10	"	31.3	"
	EMA	90			
	DVB	0.05			
5	EMA	100	"	36.5	Asymmetrical beads
	DVB	0.05			
6	MMA	90	"	31.7	Symmetrical beads
	o-Chlorostyrene	10			
	DVB	0.05			
7	MMA	10	"	29.3	"
	o-Chlorostyrene	90			
8	o-Chlorostyrene	100	"	35.3	"
9	Vinylbenzyl chloride	100	"	35.4	"
10	MMA	90	Neohexane	29.8	"
	Acrylonitrile (VCN)	10			
	DVB	0.025			
11	MMA	50	"	28.4	"
	VCN	50			
	DVB	0.025			
12	MMA	90	"	29.9	"
	p-tertiary butyl styrene	10			
	DVB	0.05			
13	MMA	70	"	39.6	< 50 sym.
	p-tertiary butyl styrene	30			> 50 asym.
14	MMA	80	Neopentane	31.3	Symm.
	Vinyl acetate (VA)	20			
	DVB	0.05			
15	MMA	10	"	31.2	"
	VA	90			
16	MMA	90	"	31.05	"
	Butyl acrylate (BA)	10			
	DVB	0.05			

Example	Monomers	Parts	Blowing Agent	Volume Percent	Result
17	MMA	100	Neopentane	39.55	Asym.
18	"	"	Isopentane	21.1	Asym.
19	"	"	"	27.3	Sym.
20	DVB	0.05	Dichlorotetrafluoroethane (DCTFE)	25.4	"
21	Styrene DVB	100 0.05	Neopentane	38.8	Asym.
22	Styrene DVB	100 0.05	DCTFE	61.4	"
23	Styrene Ethylene glycol dimethacrylate (EGD)	100 0.2	Neohexane	37.45	"
24	Styrene	100	Neopentane	23.0	Major Asym.
25	Styrene Methacrylic Acid (MMA)	99 1	"	23.0	Sym.
26	Styrene MAA	96 4	"	33.0	Major Sym.
27	Styrene MAA	84 16	"	33.0	Major Asym.
28	Styrene MAA VBC DVB	83 2 15 0.05	"	39.44	Sym.
29	Styrene Acrylic Acid (AA)	99 1	"	38.8	"
30	Styrene AA EGD	98 2 0.12	"	34.05	Sym.
31	Styrene MAA DVB	98 2 0.05	DCTFE	36.6	Sym.
32	Vinylidene Chloride (Vc Cl <sub>2</sub> ) VCN	91 9	Neopentane	36.6	Sym.
33	VA MMA	70 30	"	31.2	"
34	VA	100	"	31.2	"

Example	Monomers	Parts	Blowing Agent	Volume Percent	Result
35	MMA AA	98 2	Isobutylene	26.8	Sym.
36	MMA AA	98 2	n-Butane	3.85	"
37	Styrene MAA DVB	98 2 0.05	1,1-dichlorotetra- fluoroethylene	38.0	"
38	Styrene MAA	99.6 0.4	Neopentane	33	80% Asym.
39	o-Chlorostyrene MAA DVB	92 8 0.05	"	37.8	Sym.
40	Styrene VCN	95 2	"	33.0	80% Sym.
41	Styrene VCN	90 10	"	38.0	Sym.
42	Styrene VCN	20 80	"	38.0	Sym.
43	Styrene	60	"	12.8	Major Sym.
	VCN	40	"		Some Asym.
44	Styrene	60	"	6.8	No en- capsulation
	VCN	40	"		
45	Vinyl chloride (VCI) VeCl <sub>2</sub>	30.6 45.6	"	30.4	Sym.
46	MMA VeCl <sub>2</sub>	100—10 90—0	"	34—39.5	Sym.
47	Methyl Acrylate	100	Neohexane	59.5	Sym.
48	Methyl Acrylate	100	"	32.9	"
49	MA MMA	90—70 10—30	Isopentane	31—33.8	Sym.
50	MMA EGD	90 10	Neopentane	60—96.5	Sym.
51	VeDI <sub>2</sub> BA	80 20	"	32	Sym.
52	MA VCN	10—90 90—100	"	30.8—33.9	Sym.

**EXAMPLE 53**

A polymerization reaction was charged with 100 parts of deionized water and 15 grams of a 30 percent by weight colloidal silica dispersion. To this mixture was added 2 1/2 parts of a copolymer prepared from diethanol amine and adipic acid in equimolar proportions to give a product having a viscosity of about 5 centipoises at 25°C. One (1) part of a solution containing 2 1/2 percent potassium dichromate was added to the polymerization reactor. The pH of the aqueous mixture was adjusted to 4 by addition of hydrochloric acid. Seventy-seven (77) parts of a monomer mixture comprising 70 percent by weight of acrylonitrile and 30 percent by weight of vinylidene chloride was catalyzed with one-half to 1 percent of 2,2'-azobis(isobutyronitrile). To this monomer mixture was added 23 weight percent (30.3 volume percent) based on the weight of the oil phase of neopentane. The reaction mixture was subjected to violent agitation by a blade rotating at a speed of about 10,000 rpm. A portion of the contents was sampled to determine particle size and the reactor immediately sealed. The monomer neopentane droplets appeared to have diameters ranging from about 2 to about 5 microns. The reaction mixture was maintained at a temperature of about 55°C. for a period of 24 hours. Gentle agitation was maintained during this reaction period and at the end of the reaction period, the temperature of the mixture was lowered to about 30°C. The reaction mixture had a chalky-white appearance similar to milk. A portion of the mixture was filtered to remove the small beads and the beads subsequently placed in an air oven at a temperature of about 30°C. A portion of the beads was heated to a temperature of about 150°C. for a period of about 2 minutes. At this temperature the beads expanded and turned dark. The product, prior to heating, appeared under a light microscope to have a fine structure to the surface, and contained a liquid centre of neopentane.

**EXAMPLE 54**

Beads prepared in accordance with Example 1 were confined within a mold in a quantity sufficient to fill the mold when expanded. They were heated to a temperature of about 140°C. for a period of three minutes. The mold and contents were cooled and the resultant article was found to conform to the smooth configuration of the mold. It had a white appearance and the tiny cells were not readily detectable by means of the naked eye. It was strong, durable and apparently had a smooth surface. On microscopic examination the individual particles appeared to be tightly bonded together, each forming an individual cell.

**EXAMPLE 55**

Expanded polymethyl methacrylate particles prepared in accordance with Example 1 and

having diameters of 2-3 microns and a void to polymer ratio of approximately 20:1 i.e., a bulk density of approximately 0.06 were admixed with water in a ratio of 15 parts by weight of particles to 85 parts of water. Fifty-eight parts of the resultant dispersion were admixed with 28.6 parts of a synthetic resinous latex prepared from 67 parts by weight of ethyl acrylate and 33 parts by weight of methyl methacrylate. This latex was 50 percent solids. 13.5 Parts of a 2 percent by weight hydroxypropylmethyl cellulose solution was added to the latex expanded particle dispersion. The methyl cellulose served as a viscosity controlling agent to permit brushing. The resultant material was then brushed on to a half inch diameter (1.27 mm.) copper tube and permitted to air dry. This procedure was repeated resulting in a coating about 8 mils (0.2 mm.) in thickness. A portion of the half inch copper tube was coated with the latex alone until a coating thickness of 8 mils (0.2 mm.) was obtained (dry thickness). Water at a temperature of about 1 to 2°C. was then pumped through the tube while the tubing was maintained in a room having a temperature of about 22°C. The surface temperatures of the coated and uncoated tubing were measured by means of a surface pyrometer. The bare copper surface temperature at the inlet and outlet of the tube measured 4 1/2° and 5 1/2°C. respectively. The latex coating measured about 9°C. whereas the surface of the coating containing the expanded particles measured 18 1/2°C.

**EXAMPLE 56**

A portion of the coating composition of Example 55 employing the expanded particles was applied to bond paper and permitted to air dry at about 24°C. to result in a coating about 5 mils in thickness. The resultant coating almost totally obscured printing on the bond paper, adhered well to the paper, and provided an insulating coating thereon.

**EXAMPLE 57**

A coating composition was prepared utilizing unexpanded dry particles as prepared in Example 1, wherein 50 parts by weight of the particles were admixed with 122 parts of an aqueous latex, 41 percent solids which was prepared by utilizing 50 percent by weight methyl methacrylate, 46 percent by weight normal butyl acrylate and 4 percent by weight acrylic acid. Two coatings of this formulation were applied to the outer wall of a paper cup with air drying between the coats and after the last coat. On heating the cup to a temperature of 130°C. a white opaque foam coating was obtained which provided adequate insulation for hot beverages such as coffee. No tendency was observed for the coating to peel or otherwise be removed from the cup.

## EXAMPLE 58

In a manner similar to the foregoing example, utilizing the 70:30 copolymer of methyl acrylate and methyl methacrylate, a thin plastic cup made from a graft copolymer of 95 percent styrene on polybutadiene rubber was similarly coated and subsequently expanded at 70°C. to provide commensurate beneficial results.

## EXAMPLE 59

The coating composition of Example 58 was brushed over the entire outside surface of a paper cup and the inside of an identical paper cup until a coating thickness of about 5 mils (0.13 mm.) was obtained on each cup. The cups were then nested with the coated surfaces adjacent and facing each other. The nested cups were placed in an air oven at 140°C. The coatings expanded, and fused together forming a rigid unitary article. The resultant laminated cup was strong and rigid. Similar beneficial results were obtained when sheets of paper were treated in a similar manner and the coatings foamed in contact with each other.

## EXAMPLE 60

The procedure of Example 58 was repeated wherein the various binders were employed including a latex about 45 percent solids prepared by polymerizing 40 percent styrene and 60 percent 2-ethylhexyl acrylate, a latex about 40 percent solids prepared by polymerizing 15 parts of styrene, 55 parts of isobutyl acrylate, and 30 parts of acrylic acid, a latex prepared by polymerizing 60 parts of styrene and 33 parts of butadiene.

## EXAMPLE 61

A coating composition was prepared using 166 parts by weight of a suspension of the expandable particles prepared in Example 1 wherein the solids concentration was 30 percent by weight, 120 parts by weight of a latex, 41.7 percent solids and prepared by the copolymerization of 40 parts of styrene and 60 parts of 2-ethylhexyl acrylate, and 15 parts by weight of a 5 percent by weight solution of a sodium polyacrylate commercially available under the trade designation of "Acrysol GS". ("Acrysol" is a registered Trade Mark). This coating formulation was applied to a wooden panel which had been previously coated with two coats of a blue colored lacquer. This coating adhered well to the surface, showed no tendency to crack or peel therefrom, but on heating with a blast of hot air the particles in the coating expanded, and the coating released from the surface leaving the clean surface of the blue lacquer. In a similar manner, metal panels were coated with the above-mentioned composition and dried to provide a continuous protective film. On heating of the coatings they released from the surface to leave a clean metal surface.

## EXAMPLE 62

A mixture was prepared utilizing 200 parts of a 55 percent solids natural rubber latex, 50 parts by weight of dry unexpanded particles prepared in accordance with Example 1, two parts of a rubber anti-oxidant solid under the trade designation of "Wingstay S" and 50 parts by weight of water. ("Wingstay" is a registered Trade Mark). These components were mixed to a uniform dispersion and coagulated by the addition of hydrochloric acid while agitating. When this dispersion was completely coagulated, the coagulum was separated and vacuum dried at about 23°C. for 48 hours. A rectangular portion was cut from the dried mass having the relative dimensions of 1, 2 and 4 and placed in an air oven at a temperature of 165°C. for 5 minutes. An enlarged replica of the original piece was formed which had a density of 18.3 pounds per cubic foot (292 kg./cu.m.). It was observed that the expanded material was stiffer than prior to expansion while still retaining elastomeric characteristics. The compressive strength of the expanded material was significantly higher than most sponge rubbers. Microscopic examination of sections of the body indicated that the expandable particles maintained their identity. Other samples of the above-delineated composition were foamed by means of dielectric heat to densities of about 14 pounds per cubic foot (224 kg./cu.m.). The unexpanded portions varied in thickness from about 1/4 of an inch to one inch (0.63 to 2.5 cm.).

## EXAMPLE 63

One hundred parts by weight of an epoxy resin composition was prepared utilizing a mixture of a condensation product of Bisphenol A and epichlorohydrin under the designation of D.E.R. 331 (Registered Trade Mark), 3 parts by weight of water, 12 parts by weight of triethylenediamine and 16 parts by weight of dry particles prepared in accordance with Example 1. Mixing of the above components resulted in a foamable material that expanded to a rigid foam having a density of about 2 pounds per cubic foot (32 kg./cu.m.). An alternate method of formulating the expandable epoxy composition is to employ a minor portion of the triethylenetetraamine such as two parts by weight of the triethylenetetraamine, a partial prepolymer is formed having a significantly increased viscosity. Subsequent addition of the remaining 10 parts of the triethylenetetraamine causes the generation of sufficient heat to expand the particles and provide a rigid epoxy foam.

## EXAMPLE 64

A polymerization reactor equipped with an agitator was charged with 100 parts of de-ionized water and 60 parts of a 30 weight percent dispersion of colloidal silica in water. The colloidal silica dispersion was 30 percent by

weight solids and is available under the trade name of "Ludox HS". To this mixture was added 10 parts of a 10 weight percent aqueous solution of a copolymer prepared from diethanol amine and adipic acid in equimolar proportions by carrying out a condensation reaction to give a product having a viscosity of about 100 centipoises at 25°C. One part of a solution containing 2.5 weight percent potassium dichromate was added. The pH of the solution was adjusted to 4 by means of hydrochloric acid. An oil phase mixture was prepared by utilizing 40 parts of neopentane and 60 parts of methyl methacrylate and one-half percent by weight of benzoyl peroxide based on the weight of the methyl methacrylate. The oil phase mixture was added to the water phase with violent agitation supplied by a blade rotating at a speed of about 10,000 rpm. the reactor was immediately sealed and a portion sampled to determine the particle size. The droplets appeared to have diameters of from about one-half to about 3 microns. After the initial dispersion the reaction mixture was maintained at a temperature of about 80°C. for a period of about 24 hours. At the end of this period the temperature was lowered and the reaction mixture had the appearance of a white milky liquid similar to a chalk-white milk. A portion of the mixture was filtered to remove the beads and the beads subsequently dried in an air oven at a temperature of about 30°C. The resultant beads had diameters of from one-half to 3 microns and showed symmetrical encapsulation. On heating to about 130°C. the beads expanded to about 2 to 3 times their original diameter. A portion of the reaction product was treated in a manner similar to Example 61 and commensurate beneficial results were achieved. However, the smaller particles tend to give a smoother, thinner coating which foams in a more uniform manner.

Generally, if symmetrical encapsulation is desired, monomer blowing agent mixtures are utilized in proportions such that polymer tends to precipitate as the polymerization of the monomer advances to about 10 percent conversion. Generally, polymers which are more soluble in the monomer-blowing agent mixture either provide minor encapsulation or asymmetric encapsulation. Where there is total solubility of the polymer in the blowing agent, no encapsulation results and only a clear bead is obtained. With particles below about 50 microns, such clear beads with no encapsulation show no tendency to foam, expand, or form the cup-like particles shown in Figure 4. Thus, a particular polymer-blowing agent composition which provides satisfactory foam when utilized in larger sections is oftentimes of no value as a blowing agent when employed with particles smaller than about 50 microns in diameter. The present invention provides a particularly advantageous and beneficial means of

preparing expandable thermoplastic, resinous particles having a relatively small size. For many applications requiring smaller particles, diameters of from 3 to 50 microns are employed. Advantageously particles having diameters of about 5 to about 20 microns provide additional benefits.

The symmetrically encapsulated particles in accordance with the present invention readily expand to form monocellular particles and are readily employed to mold and form thermoplastic, expanded cellular shaped articles composed of a multitude of such particles, in a manner generally similar to that utilized for conventional expandable thermoplastic resinous material having a larger particle size.

Expanded beads in accordance with the present invention are particularly advantageous for the preparation of aerosols or plastic smoke. The beads or particles which on expansion have a diameter below 50 microns or as little as 0.5 microns, and most beneficially from about 2 to 25 microns wherein the particles have an individual apparent density of about 0.025 are most advantageously employed. Such small particles are readily dispersed into a stream of gas, typically, air, to provide a dispersion or aerosol which does not settle out rapidly. Such aerosols are readily prepared by adding unexpanded particles to a heated gas stream at a rate sufficient to raise the temperature of the unexpanded particles to an expansion temperature or alternatively by dispersing pre-expanded individual particles in a gas stream by conventional methods. Generally when the particles are to be used for aerosols, it is preferably that a relatively large amount of blowing agent be encapsulated therein. Particularly beneficial are the blowing agent contents in a range of from 30 to 50 percent by weight of the particle.

#### WHAT WE CLAIM IS:—

1. A monocellular thermoplastic, resinous polymeric particle having a generally spherical shape and having encapsulated therein a discrete portion of a non-polar volatile liquid blowing agent which becomes gaseous at a temperature below the softening point of the polymer.
2. A particle as claimed in Claim 1 wherein the blowing agent is present in an amount not less than 20 per cent by volume based on the total volume of the polymer and blowing agent.
3. A particle as claimed in Claim 2 wherein the blowing agent is present in an amount ranging from 50 to 95 per cent by volume.
4. A particle as claimed in Claim 1 wherein the blowing agent is centrally disposed within a symmetrical shell of polymer.
5. A particle as claimed in Claim 1 having a diameter of from 3 to 50 microns.
6. A particle as claimed in Claim 5 wherein the diameter of the particle is between 5 and 20 microns.



7. A particle as claimed in any one of Claims 1, 2, 3 or 5 wherein the thermoplastic resinous material comprises polystyrene.
8. A particle as claimed in any one of Claims 1 to 6 wherein the thermoplastic resinous material comprises a polymer of methyl methacrylate.
9. A particle in accordance with any one of Claims 1 to 6 wherein the thermoplastic resinous material is a copolymer of methyl methacrylate with styrene, ethyl methacrylate, *o*-chlorostyrene, acrylonitrile, *p*-tertiary-butylstyrene, vinyl acetate, or butyl acrylate.
10. A particle in accordance with any one of Claims 1 to 6 wherein the thermoplastic resinous material is a copolymer of styrene with methacrylic acid, acrylonitrile, vinylbenzyl chloride, or acrylic acid.
11. A particle in accordance with any one of Claims 1 to 6 wherein the thermoplastic resinous material comprises a polymer of acrylonitrile and vinylidene chloride.
12. A particle in accordance with any one of Claims 1 to 6 wherein the thermoplastic resinous material is a polymer of vinylbenzyl chloride.
13. A particle in accordance with any one of Claims 1 to 6 wherein the thermoplastic resinous material is a copolymer of *o*-chlorostyrene and acrylic acid.
14. An assembly comprising a plurality of the particles claimed in Claim 4 in closely spaced adjacent relationship, a thermoplastic resinous binder surrounding at least a major portion of the particles and adhering the particles together.
15. An assembly as claimed in Claim 14 wherein the thermoplastic resinous binder is adhered to at least one surface of a substrate.
16. An assembly as claimed in Claim 15 wherein the particles and binder form a substantially continuous layer.
17. An assembly as claimed in Claim 15 or Claim 16 wherein the substrate is a fibrous cellulosic material or a thermoplastic resinous material.
18. An assembly as claimed in Claim 15 or Claim 16 wherein the substrate is a container.
19. An assembly as claimed in Claim 18 wherein the thermoplastic resinous substrate is in the form of a drinking cup.
20. An assembly comprising a plurality of the particles claimed in Claim 4 dispersed within a hardenable resinous material.
21. An assembly as claimed in Claim 20 wherein the hardenable resinous material is an exothermic material which, on curing, provides sufficient heat to cause the particles to expand.
22. An assembly as claimed in Claim 21 wherein the hardenable resinous material is an epoxy resin.
23. A coating comprising a plurality of thermoplastic resinous particles having encapsulated therein a non-polar volatile blowing agent as a distinct and separate liquid phase, the particles being adhered together by means of a flexible thermoplastic resinous binder, the binder being present in a proportion just sufficient to adhere the particles together and adhere them to a substrate.
24. A method for the preparation of monocellular expandable thermoplastic resinous polymer particles comprising dispersing a polymerizable monomer containing between 20 and 95 per cent by volume based on the volume of the oil phase of a non-polar volatile blowing agent in a non-solvent dispersing medium to form a plurality of droplets and polymerizing the droplets to form rigid generally spherical polymer shells, containing encapsulated therein a discrete, liquid phase of the non-polar volatile blowing agent.
25. A method as claimed in Claim 24 wherein the monomeric material containing the volatile blowing agent is dispersed in an aqueous dispersion medium utilizing a suspending agent adapted to give limited coalescence technique to provide a generally narrow range of particle size distribution.
26. A method as claimed in Claim 25 wherein the limited coalescence dispersion system provides droplets having a particle diameter of from 1/2 micron to 50 microns.
27. A method of preparing an expandable thermoplastic resinous particle having symmetrically encapsulated therein a quantity of a non-polar liquid volatile blowing agent comprising polymerizing methyl methacrylate in the presence of from 20 to 95 per cent based on the volume of the oil phase, of the volatile blowing agent therefor while the monomer and blowing agent are dispersed in the form of spherical droplets in an aqueous suspending medium.
28. An expanded thermoplastic resinous particle having a generally spherical cup-like configuration.
29. A particle as claimed in Claim 28 having a generally circular opening.
30. A method for the preparation of monocellular thermoplastic polymer particles substantially as described with reference to any one of Examples 1 to 43, 45 to 53 and 62 to 64.
31. Monocellular thermoplastic particles whenever prepared by the method claimed in any one of Claims 24 to 27 or 30.
32. A method of coating articles substantially as described with reference to any one of Examples 55 to 61 and 64.
33. Articles whenever coated by the method claimed in Claim 32.
34. Monocellular thermoplastic polymeric particles substantially as described with reference to Figures 1 and 2 or 3 and 4 of the accompanying drawings.
35. An assembly as claimed in Claim 14 substantially as described with reference to Figures 7 or 8 and 9 of the accompanying drawings.

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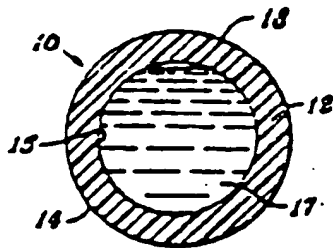


Fig. 1

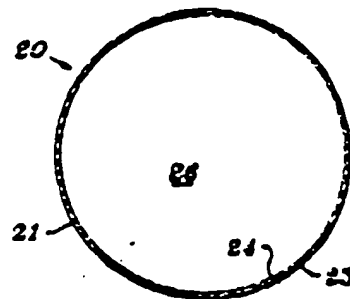


Fig. 2

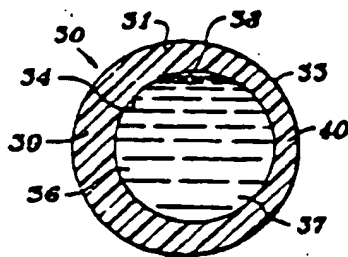


Fig. 3

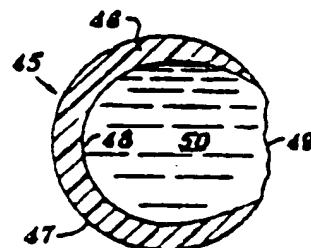


Fig. 4

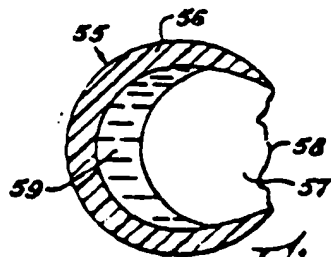


Fig. 5

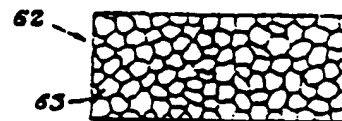


Fig. 6

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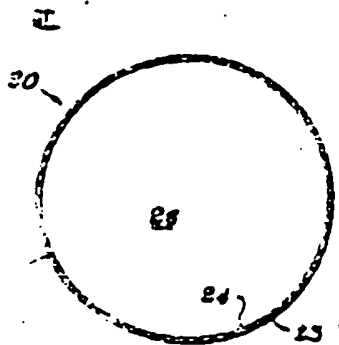


Fig. 2

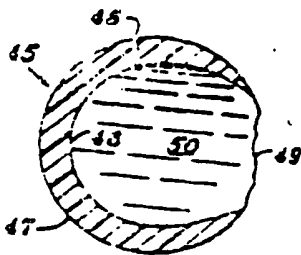


Fig. 4

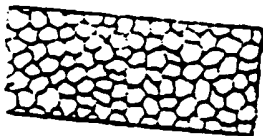


Fig. 6

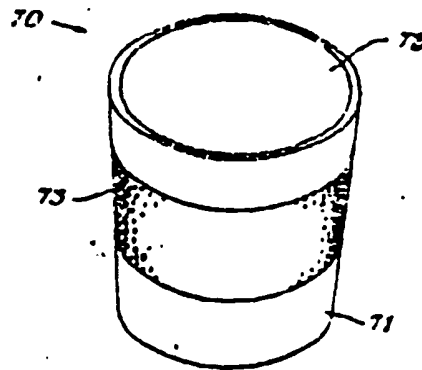


Fig. 7

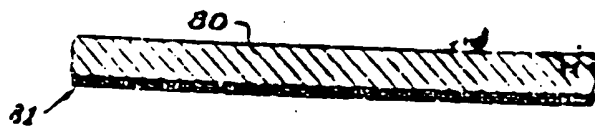


Fig. 8

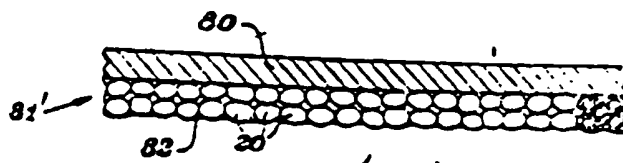


Fig. 9